

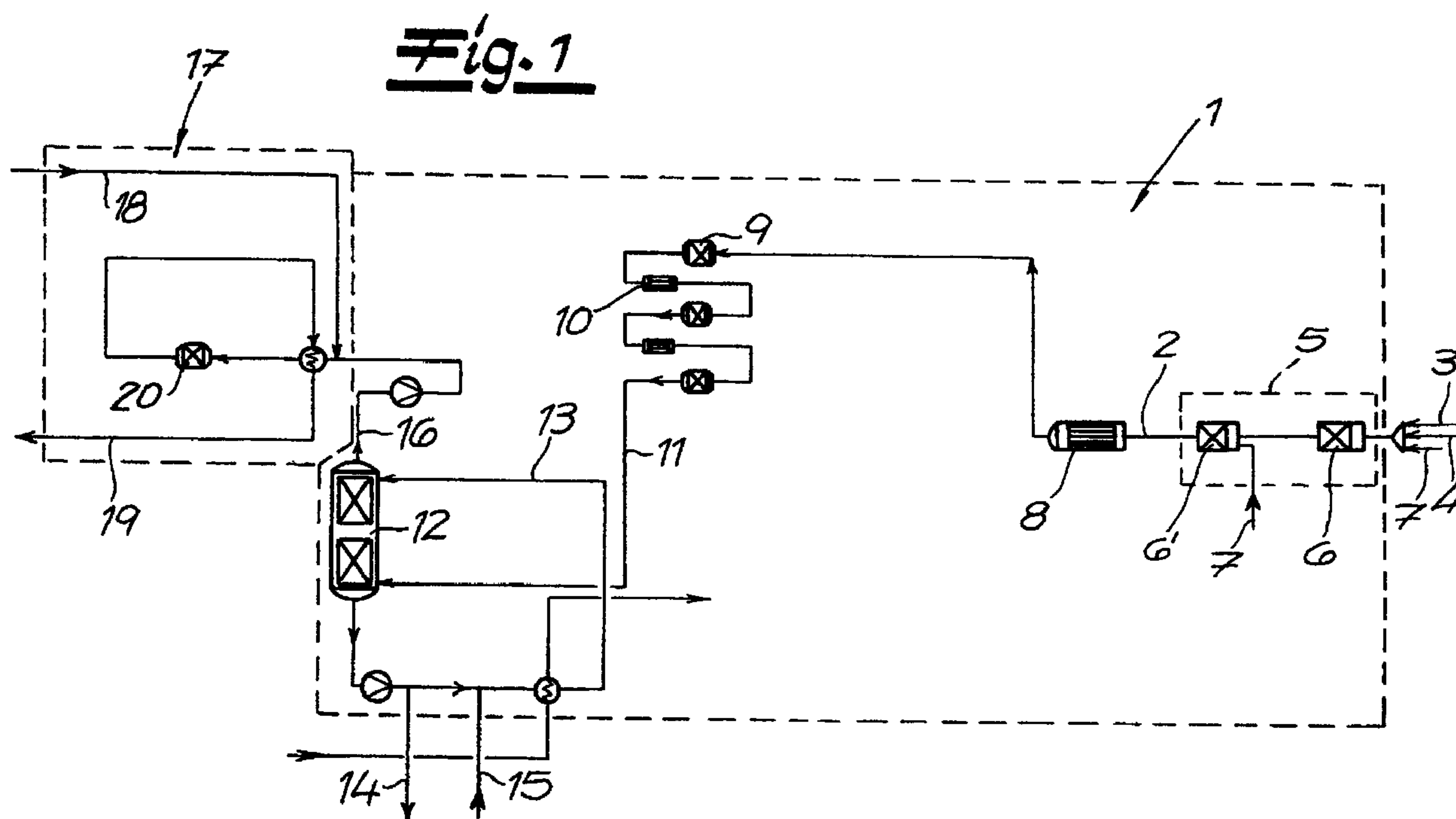


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(71) Demandeur/Applicant:
UHDE GMBH, DE
(72) Inventeur/Inventor:
THIELERT, HOLGER, DE
(74) Agent: MCFADDEN, FINCHAM

(54) Titre : PROCEDE DE PRODUCTION D'ACIDE SULFURIQUE ET INSTALLATION POUR METTRE LEDIT PROCEDE EN OEUVRE

(54) Title: METHOD OF PRODUCING SULFURIC ACID AND INSTALLATION FOR CARRYING OUT THE METHOD



(57) Abrégé/Abstract:

The invention relates to a method for producing sulphuric acid. According to the invention, a crude gas containing SO_2 is produced in a sulphuric acid recovery installation, the crude gas is conducted through at least one reaction container, in which a catalytic reaction of SO_2 into SO_3 takes place and the SO_3 formed in this process is converted into sulphuric acid. The SO_2 emission of at least one sub-stream of the gaseous stream that exits the sulphuric acid recovery installation is hydrogenated in an aftertreatment step with a gas rich in H_2 . The gaseous stream containing H_2S that is thus formed is fed to the H_2S scrubber of a coke-oven gas installation or petrochemical installation. The invention also relates to an installation for carrying out said method.



ABSTRACT

The invention relates to a method of producing sulfuric acid wherein an SO_2 -containing raw gas produced in a sulfuric-acid recovery plant is passed through at least one reactor in which a catalytic reaction of SO_2 to SO_3 takes place, and the SO_3 thereby formed is converted into sulfuric acid. According to the invention, at least a partial stream of the gas stream leaving the sulfuric-acid recovery plant is hydrogenated with an H_2 -rich gas in a post-treatment stage. The H_2S -containing gas stream formed by the hydrogenation is fed into the H_2S gas scrubber of a coke oven plant or a petrochemical plant. The invention also relates to an installation for carrying out the method. FIG. 1.

METHOD OF PRODUCING SULFURIC ACID AND INSTALLATION FOR CARRYING OUT
THE METHOD

The present invention relates to a method of producing sulfuric acid wherein an SO₂-containing raw gas is produced in a sulfuric-acid recovery plant, the raw gas is fed through at least one reactor in which the SO₂ undergoes a catalytic reaction from SO₂ to SO₃, and the SO₃ thus formed is converted into sulfuric acid.

The raw gas can be produced by combustion of catalytic conversion of hydrogen-sulfide-containing waste gases that accumulate, for example, during the purification of coke-oven gases. The raw gas mostly has an SO₂ content between 3 and 12 % (v/v). The gas is usually cooled in a waste-heat boiler and optionally diluted with air to establish a superstoichiometric O₂/SO₂ ratio. The exothermic reaction of SO₂ to give SO₃ takes place over catalysts, e.g. V₂O₅ catalysts at temperatures between 400 and 650°C. The SO₃ hereby formed is cooled and absorbed in concentrated sulfuric acid in an absorber. In the known method, which is also designated as a contact method in the literature, SO₂ and SO₃ in the form of a sulfuric-acid mist occur as substantial emissions. The SO₂ emissions result from an incomplete conversion of SO₂ to SO₃. Unconverted SO₂ is merely absorbed to a very small extent in the absorber. The SO₂ emission can be up to 3000 mg/Nm³ if suitable measures are not taken to reduce emissions.

Numerous measures for reducing SO₂ emissions are known. A high O₂/SO₂ ratio can thermodynamically promote the conversion of SO₂ at a generally lower temperature level. The use of a cesium-

doped catalyst can improve the conversion and achieve lower SO₂ emissions. Finally, in order to improve the degree of conversion, the number of catalyst stages can be increased or an intermediate absorber can be provided before the last catalyst stage. However, in some cases, the operating costs of a sulfuric-acid recovery plant are increased significantly by the measures described. Furthermore, the measures are complex in terms of process technology and plant technology and are only suitable for retrofitting existing sulfuric-acid recovery plants to a limited extent. An overview of the known measures for reducing SO₂ emissions in a sulfuric-acid recovery plant is given in the publication of H. Wiesenberger "State of the art in sulfuric acid production," Monographs, Vol. 137 (2001), pages 7 to 23, ISBN 3-8557-583-1.

Gypsum suspension scrubbers are used to separate SO₂ in power plants, waste incineration plants and industrial installations where a high degree of separation is achieved. In coking plants or petrochemical plants having a downstream sulfuric-acid recovery plant, a gypsum-suspension scrubber is not generally available. The SO₂ emission cannot be introduced into the H₂S scrubbers of a purification plant for coke-oven gas or corresponding gas scrubbers in a petrochemical plant since the salts produced interfere with the downstream stages of a conventional coke-gas purification system or corresponding equipment in a petrochemical plant.

German patent 26 58 208 discloses a method of eliminating sulfur oxides from a waste gas produced during the combustion of

hydrocarbons in which sulfur oxides contained in the waste gas are reduced to hydrogen sulfide in a catalytic conversion zone. The hydrogen sulfide is extracted from the waste gas stream so that the purified waste gas stream only contains small quantities of sulfur.

5 It is known from US patent 2,992,884 to reduce residual gases from sulfuric acid production with hydrogen.

In a method known from German patent document 21 66 916 [GB 1,344,471], waste gases are purified by catalytic hydrogenation of sulfur, the sulfur dioxide contained in the waste gases being
10 converted into H_2S using a stoichiometric quantity of hydrogen and into sulfur following absorption in an aqueous alkaline solution.

US patent 4,919,912 describes a method in which a SO_2 -containing gas stream is passed through a reaction zone in which a Claus reaction takes place and elemental sulfur is formed. Since
15 the gas stream contains a superstoichiometric quantity of SO_2 for the Claus reaction, the waste gas from this Claus reaction is fed to a hydrogenation zone in which the excess SO_2 is converted into hydrogen sulfide. The hydrogen sulfide is extracted from the outflowing gas and fed back to the reaction zone and is available
20 for producing sulfur with the Claus reaction.

The object of the invention is to eliminate the SO_2 emissions that occur in a sulfuric-acid recovery plant as completely as possible. In particular, it should be possible to retrofit existing sulfuric-acid plants in coking operations and
25 petrochemical plants by using the gas scrubbers available there. In the planning of new plants, the method should contribute toward

being able to produce concentrated sulfuric acid having a high yield and energy efficiency.

The subject matter of the invention and the solution that attains this object is a method of producing sulfuric acid in which an SO₂-containing raw gas is produced in a sulfuric-acid recovery plant, the raw gas is passed through at least one reactor in which a catalytic reaction of SO₂ to SO₃ takes place, and the SO₃ thereby formed is converted into sulfuric acid, wherein, in order to reduce the SO₂ emission of the gas stream leaving the sulfuric-acid recovery plant, at least a partial stream of the SO₂-containing gas leaving the sulfuric-acid recovery plant is hydrogenated with an H₂-rich gas and the H₂S-containing gas stream formed by the hydrogenation is fed into a H₂S gas scrubber of a coke-oven plant or a petrochemical plant. In the method according to the invention, the H₂S-containing gas stream is fed back to H₂S gas scrubbers usually provided for gas purification in coking plants and in petrochemical plants. The method according to the invention is suitable for retrofitting existing sulfuric-acid recovery plants in coking operations and petrochemical plants and allows almost emission-free operation of the sulfuric-acid recovery plant with respect to gases.

If the sulfuric-acid recovery plant is part of a coking plant operation, coke-oven gas can be used for hydrogenating the SO₂ emission. Furthermore, it is also possible to recycle the H₂S-containing gas formed by hydrogenation back to the H₂S gas scrubber of a purification plant for coke-oven gas.

The gas stream is preferably heated by heat exchange with the gas stream leaving the hydrogenating reactor before entering a hydrogenating reactor.

5 The SO₂-containing raw gas can be produced by combustion or catalytic conversion of hydrogen-sulfide containing gases that accumulate in particular during the purification of coke-oven gas. According to a preferred embodiment of the method according to the invention, the gas stream leaving the sulfuric-acid recovery plant with SO₂ emissions is divided into first and second partial
10 streams, the first partial stream being recycled to the SO₂-containing raw gas and the second partial stream being fed to the previously described post-treatment stage and hydrogenated with H₂-rich gas. The sulfuric-acid yield can be improved by partially recycling the gas stream leaving the sulfuric-acid recovery plant
15 back to the SO₂-containing raw gas stream. The partial recycling of the SO₂ emissions into the raw gas according to the invention has the further advantage that a lower degree of conversion of the catalytic reaction of SO₂ to SO₃ can be tolerated, specifically while maintaining good efficiency for the sulfuric-acid recovery.
20 Furthermore, as a result of recycling part of the SO₂ emission back to the raw gas, a lower water content is established in the raw gas that promotes the concentration of the sulfuric acid and can be used to obtain a highly concentrated sulfuric acid.

A further advantageous embodiment of the method according
25 to the invention provides that the SO₂-containing raw gas is produced by a two-stage combustion of hydrogen-sulfide-containing gases and that the first partial stream is fed to the raw gas

before that of the second combustion stage. The SO_3 formed by the catalytic conversion of SO_2 is appropriately absorbed in an absorber in concentrated sulfuric acid.

The invention also relates to a plant according to claim 8 for carrying out the method. Claims 9 to 11 describe preferred embodiments of this plant.

The invention is explained hereinafter with reference to an illustrated embodiment. In the figures:

FIG. 1 is a flow chart of the method according to the invention,

FIG. 2 shows the method of FIG. 1 with an additional partial return of the SO_2 emission into the SO_2 -containing raw gas.

A sulfuric-acid recovery plant 1 in which SO_2 -containing raw gas 2 is initially produced is assumed. The SO_2 -containing raw gas 2 is produced by superstoichiometric combustion of a hydrogen-sulfide-containing waste gas 3 that is fed to a combustion furnace 5 with an air stream 4 containing acidic gas components. In the illustrated embodiment, combustion is carried out in two successive combustion chambers 6 and 6' where the gas stream for establishing a superstoichiometric O_2/SO ratio is optionally diluted with air 7. The hot SO_2 raw gas 2 is cooled in a cooler 8 and fed to a plurality of reactors 9 connected in series, in which an exothermic catalytic reaction from SO_2 to SO_3 takes place, for example, with V_2O_5 catalysts. Between the stages the gases are cooled by heat exchangers 10 to the inlet temperature of the next catalytic stage. An SO_2 -rich gas stream 11 is formed that is supplied to an absorber 12 operated with concentrated sulfuric acid. A liquid circuit 13

for the sulfuric acid is provided for the absorber 2. It is withdrawn from the bottom of the absorber 12, cooled and returned at the top. The SO_2 from the gas is absorbed in the concentrated sulfuric acid. A partial stream 14 of the sulfuric acid
5 corresponding to the absorbed quantity is discharged as a product stream. Water 15 can be supplied to the liquid circuit to adjust the sulfuric-acid concentration.

The gas stream 16 leaving the absorber 12 contains SO_2 emissions. Depending on the design of the catalytic stages 9,
10 levels can be up to 3000 mg/Nm^3 . The gas stream 16 leaving the sulfuric-acid recovery plant 1 with SO_2 emissions is hydrogenated in a post-treatment stage 17 with an H_2 -rich gas 18 in the method shown in FIG. 1. The H_2S gas stream 19 formed by the hydrogenation is returned to the scrubbing process of a coke oven plant or
15 petrochemical plant not shown, located upstream of the sulfuric-acid recovery plant 1.

Coke-oven gas containing as its main components H_2 , CH_4 and smaller quantities of CO , C_xH_x and CO_2 is used for hydrogenating the SO_2 emission. The H_2S -containing gas 19 formed by hydrogenation
20 is recycled to the H_2S gas scrubber of a purification plant for coke-oven gas.

Before entering the hydrogenating reactor 20, the gas stream 16 is preheated by heat exchange with the gas stream leaving the hydrogenating reactor 20.

25 The method variant shown in FIG. 2 differs from the method shown in FIG. 1 in that the gas stream 16 leaving the sulfuric-acid recovery plant 1 with SO_2 emissions is divided into

two partial streams 21 and 21', the first partial stream 21 being recycled to the SO₂-containing raw gas 2 and the second partial stream 21' being hydrogenated with the H₂-rich gas 18 in the post-treatment stage 17. In the illustrated embodiment according to a preferred embodiment of the invention, the SO₂-containing raw gas is produced by two-stage combustion of hydrogen-sulfide-containing gases and the first partial stream 21 is fed to the raw gas before the second combustion stage 6'.

The invention also relates to an installation for carrying out the method.

CLAIMS

1. A method of producing sulfuric acid wherein an SO₂-containing raw gas (2) produced in a sulfuric-acid recovery plant (1) is passed through at least one reactor (9) in which a catalytic reaction of SO₂ to SO₃ takes place, and the SO₃ thereby formed is converted into sulfuric acid, and wherein in order to reduce the SO₂ emission of the gas stream (16) leaving the sulfuric-acid recovery plant (1), at least a partial stream of the SO₂-containing gas leaving the sulfuric-acid recovery plant (1) is hydrogenated with an H₂-rich gas (18) and the H₂S-containing gas stream (19) formed by the hydrogenation is fed into a H₂S gas scrubber of a coke oven plant or a petrochemical plant.

2. The method according to claim 1, characterized in that coke-oven gas is used for hydrogenating the SO₂ emissions.

3. The method according to one of claims 1 or 2, characterized in that before entering into a hydrogenating reactor (20) the gas stream is heated by heat exchange with the gas stream leaving the hydrogenating reactor (20).

4. The method according to one of claims 1 or 3, characterized in that the SO₂-containing raw gas (2) is produced by combustion or catalytic conversion of hydrogen-sulfide containing gases (3) that accumulate in particular during the purification of coke-oven gas and that the gas stream (16) leaving the sulfuric-

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acid recovery plant (1) with SO₂ emissions is divided into first and second partial streams (21 and 21'), the first partial stream (21) being recycled back to the SO₂-containing raw gas (2) and the second partial stream (21') being fed to the post-treatment stage (17) and hydrogenated with H₂-rich gas (18).

5. The method according to claim 4, characterized in that the SO₂-containing raw gas (2) is produced by two-stage combustion of hydrogen-sulfide-containing gases (3) and that the first partial stream (21) is mixed with the raw gas (2) before the second combustion stage (6').

6. The method according to one of claims 1 to 5, characterized in that the SO₃ formed by the catalytic conversion of SO₂ is absorbed in an absorber (12) in concentrated sulfuric acid.

7. An installation for carrying out the method according to one of claims 1 to 6, comprising

a sulfuric-acid recovery plant (1) having at least one reactor (9) for catalytic reaction of SO₂ to SO₃ and an absorber (12) operated with sulfuric acid, and

a post-treatment stage (17) to which at least one partial stream of the gas stream (16) leaving the sulfuric-acid recovery plant can be supplied, the post-treatment stage (17) including a hydrogenating reactor (20) supplied with an H₂-rich gas for hydrogenating the SO₂ emissions of the supplied gas stream, the H₂S-containing gas stream (19) formed by the hydrogenation being fed to a gas scrubber connected to the post-treatment stage, the gas

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scrubber being a component of a purification plant for coke-oven gas.

8. The installation according to claim 7, characterized in that the post-treatment stage (17) comprises a heat exchanger
5 for preheating the gas stream before entering into the hydrogenating reactor (20) by heat exchange with the gas stream leaving the hydrogenating reactor (20).

9. The installation according to claim 7 or 8, characterized in that the sulfuric-acid recovery plant (1)
10 comprises a combustion furnace (5) in which an SO₂-containing raw gas (2) is produced by combustion or catalytic conversion of hydrogen-sulfide containing gases and that a recycling device is provided that returns a partial stream (21) of the gas stream leaving the sulfuric-acid recovery plant with an SO₂ emission to
15 the SO₂-containing raw gas.

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Fig. 1

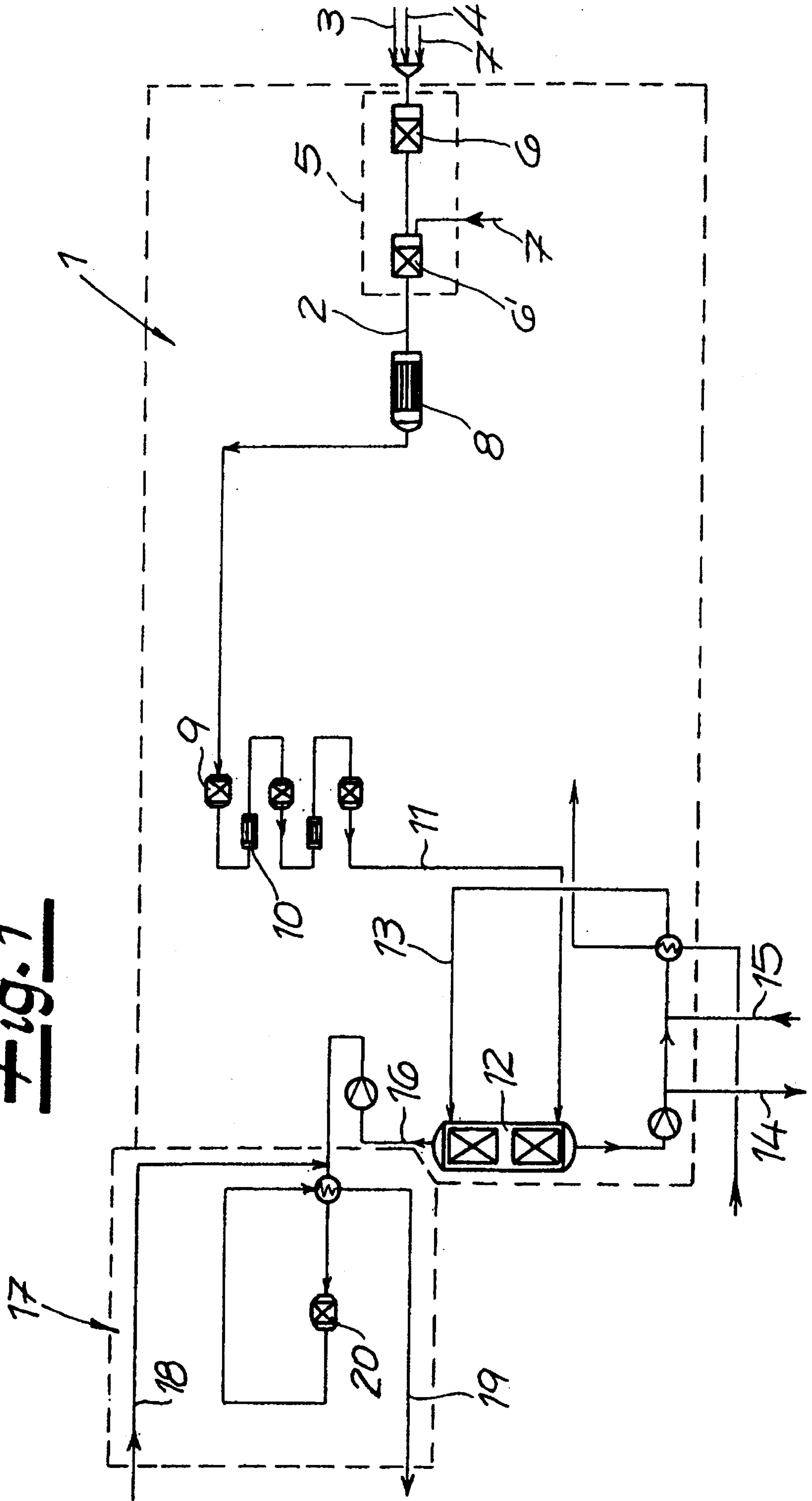


Fig. 2

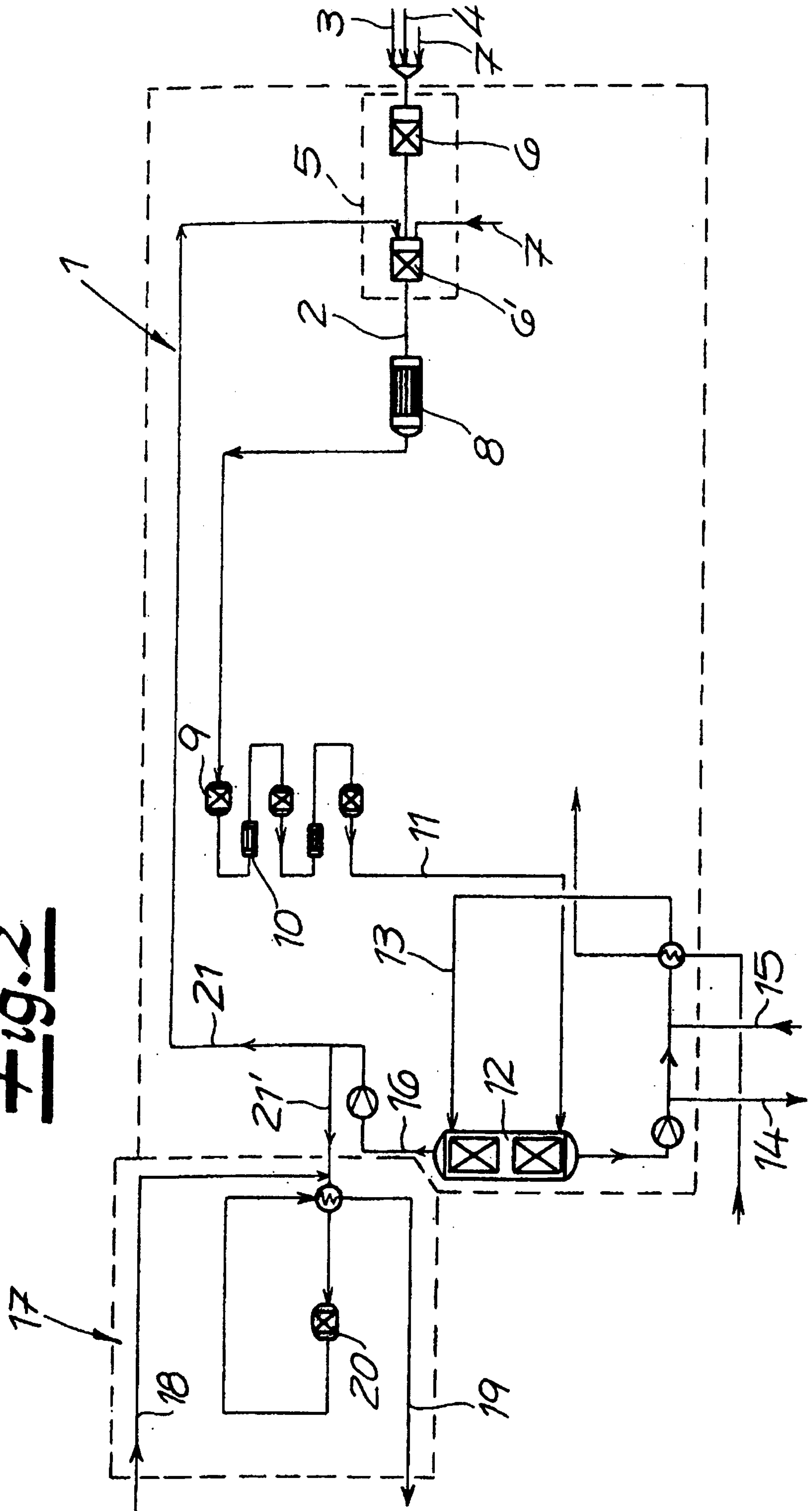


Fig. 1

